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THE CONVERSION OF SMALLER BORANE FRAGMENTS TO LARGER
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OF CHEMISTRY R W PARRY ET AL 31 DEC 84

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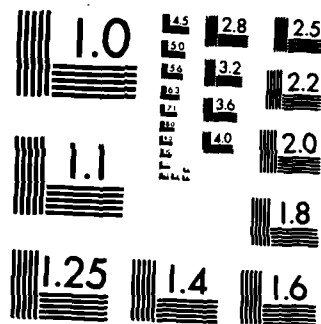
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The synthesis and reaction chemistry of B_4H_6 adducts of strong bases including trimethylphosphine, the boron framework expansion through the use of $B_2H_4 \cdot 2PMe_3$, the synthesis of polyboron cations including $B_3H_6 \cdot 2PMe_3^+$ and $B_4H_7 \cdot 2PMe_3^+$, and the coordination chemistry of $B_2H_4 \cdot 2PMe_3$ are summarized. Described also are the synthesis of isomers of dichloroborylpentaborane(9), the reaction chemistry of $B_3H_7PH_3$, anomalies in the reaction of B_4H_{10} with bases, the deuteration of triborane adducts and the deprotonation of B_5H_9 with solid KOH.		

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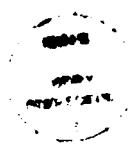
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d-; Phosphine-triborane; phosphine-tetraborane; Hexahydrobis(trimethylphosphine)-triboron(1+); Heptahydrobis(trimethylphosphine)tetraboron(1+); Tetraborane(10), reactions with Lewis Bases.

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THE CONVERSION OF SMALLER BORANE FRAGMENTS
TO LARGER STRUCTURES — SYSTEMATICS OF
BORON HYDRIDE REACTIONS

FINAL REPORT

ROBERT W. PARRY

AND

GOJI KODAMA

December 31, 1984

U.S. ARMY RESEARCH OFFICE

{ DAAG 29-76-G-0120 }
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THE UNIVERSITY OF UTAH
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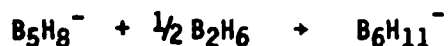
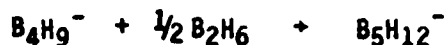
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I. Background and Objectives

Stock's early syntheses of boron hydrides involved the reaction of a rather poorly defined magnesium boride with aqueous phosphoric acid.¹ Miserable yields of a hydride mixture containing large percentages of higher hydrides were obtained. All subsequent procedures, based largely on the work of Schlesinger, Brown, Burg, and their coworkers^{2,3} as well as some commercial programs,⁴ gave B_2H_6 as the sole initial product. Higher boranes (particularly those needed for the synthesis of carboranes) are currently made from diborane by thermolysis. Through proper selection of reaction conditions and equipment B_4H_{10} , B_5H_9 , B_5H_{11} , or $B_{10}H_{14}$ can be prepared in fair to good yields,⁵ but the processes are very difficult and expensive commercial operations. Three other rather generalized processes for converting B_2H_6 to higher hydrides have been of interest in recent years. The first of these,⁶ builds on earlier work of Hough, Marshall, Hunt, Hefferan, Adams, and Makhoul⁷ of Callery Chemical Company. The processes involved the pyrolysis of $[R_4N]BH_4$ to yield $[R_4N]_2B_{10}H_{10}$. This is followed by the opening of the $B_{10}H_{10}^{-2}$ cage with HCl in liquid $(C_2H_5)_2S$ to give $B_{10}H_{12} \cdot 2S(C_2H_5)_2$. From the latter diethyl sulfide adduct, carboranes can be obtained. Yields are marginal.

A second process involves the reaction of $NaBH_4$ with B_2H_6 . Following the early work of Hough and Edwards⁸ on the reactions of B_2H_6 with sodium amalgam to give $NaBH_4$ and NaB_3H_8 , Gaines showed clearly that B_2H_6 reacts directly with $NaBH_4$ to give NaB_2H_7 and NaB_3H_8 .⁹ Muetterties carried the process further¹⁰ and obtained $NaB_{11}H_{14}$ from $NaBH_4$ and B_2H_6 under different conditions. This general process has been developed beautifully in a fundamental sense by Shore and his students who have been able to build up large borane anions in a

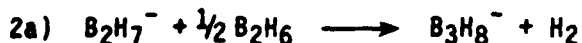
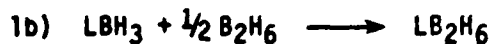
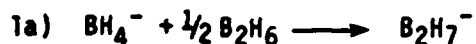
stepwise fashion by adding a borane group (Lewis acid) to a B-B bond in selected boron hydride anions.¹¹ Reactions such as those shown here were carried out:



Addition of a proton to the anion generated a neutral borane containing one boron more than the starting material. In some cases H_2 was lost. A related process was developed in recent years by Dunks and Ordóñez¹² at Union Carbide.

Shore and his coworkers further developed a new, systematic syntheses of B_2H_6 , B_4H_{10} , B_5H_{11} , and $\text{B}_{10}\text{H}_{14}$ which involves the use of polyboron anions.¹³ A hydride is abstracted from the anion (BH_4^- , B_3H_8^- , B_4H_9^- , or $\text{B}_9\text{H}_{15}^-$) by use of a Lewis acid BX_3 , and the resulting neutral borane species combines with BH_3 which is available from another source. The yields are excellent, and this process is the most convenient laboratory method presently available for the preparation of higher boranes.

The last process of interest might be considered a more generalized form of the foregoing reactions involving borane anions and diborane. If one replaces a hydride of BH_4^- with a general Lewis base, the molecule LBH_3 is formed, where L is a ligand or base such as R_3P , R_3N , or R_2S . This species, like BH_4^- , will also pick up BH_3 to give larger borane units. For example, the following reactions can be compared:



This process has some literature precedent. Some years ago Muetterties¹⁰ reported that the reaction of $(\text{CH}_3)_2\text{S}$ with B_2H_6 at 70°C gives $\text{B}_9\text{H}_{13}\cdot\text{S}(\text{CH}_3)_2$.

Several other conversions of similar type have also been reported.

In 1962 Burg¹⁴ reported that hexamethylenetetramine and several other Lewis bases act catalytically in the conversion of B_5H_{11} to B_6H_{10} , B_9H_{15} , and $B_{10}H_{14}$. In considering this process it is reasonable to postulate that B_5H_{11} reacts initially with a Lewis base to give an adduct of general form LB_xH_y which can then react with additional B_5H_{11} (or another base borane adduct in the system) to give boron framework expansion. The reaction between B_5H_{11} and Lewis bases was thus of considerable importance in delineating the path for the expansion of the boron framework. Earlier reports on the reaction of B_5H_{11} with bases such as NR_3 had described a confusing process from which no base-borane products could be characterized.¹⁵ Thus our initial work focussed on the reactions of B_5H_{11} with Lewis bases. Subsequent work involved a study of the reactions of the products obtained from the base reaction with BH_3 units or other boron sources. The goal of the study was an expansion of the boron framework.

II. Summary of the Results

Points from earlier work in this laboratory which are pertinent to the problem of boron framework expansion are emphasized. Details of past work are available in publications which are listed elsewhere in this report. A total of 21 papers describing scientific developments resulting from ARO sponsorship have been published.

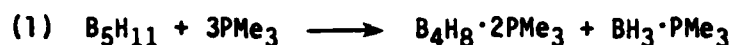
A. The Synthesis, Characterization, and Reaction Chemistry of Base

Addition Compounds of B_4H_8 .

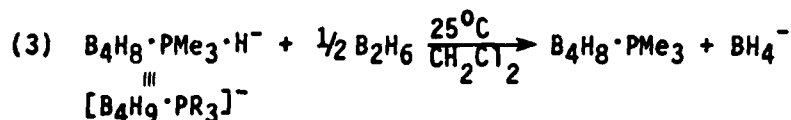
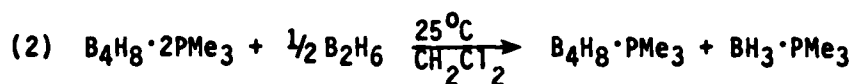
Because of the reported ability of bases such as hexamethylenetetramine and trimethylamine to catalyze the conversion of B_5H_{11} to higher boranes the reaction of B_5H_{11} with Lewis bases was studied in some detail. The arguments of symmetrical double bridge cleavage suggested that the B_5H_{11} molecule should be broken into $BH_3 \cdot NMe_3$ and $B_4H_8 \cdot NMe_3$ by trimethylamine. Still all attempts reported in the literature to recover $B_4H_8 \cdot NR_3$ from the $B_5H_{11} \cdot NR_3$ reaction system had been unsuccessful. On the other hand, Burg and Spielman¹⁶ had isolated H_3BCO and H_8B_4CO from the reaction between B_5H_{11} and CO. The two foregoing facts suggested that weak bases such as CO could form isolatable B_4H_8 complexes, but strong bases such as trimethylamine would degrade the B_4H_8 fragment to give species such as $BH_3 \cdot NMe_3$ and $(H-B)_n$ units. Given the foregoing hypothesis the isolation and characterization in this laboratory of $B_4H_8 \cdot NMe_3$ ¹⁷ and $B_4H_8 \cdot N_4(CH_2)_6$ ¹⁸ as fairly stable, white crystalline solids were of singular importance. Contrary to all earlier beliefs, it was shown that adducts of the form B_4H_8 base are very stable toward Lewis bases, but are very sensitive toward Bronsted acids. This acid sensitivity is so high that the Bronsted acidity of B_5H_{11} itself appears enough to degrade the base-

borane, $B_4H_8 \cdot NMe_3$ compound. Thus to avoid the presence of free B_5H_{11} and $B_4H_8 \cdot NR_3$ in the same vessel B_5H_{11} must be added slowly to the solution containing the free base. From this system stable $B_4H_8 \cdot NR_3$ can be isolated. If, however, NR_3 is added to a solution containing free B_5H_{11} , the $B_4H_8 \cdot NR_3$ is degraded immediately by excess B_5H_{11} . This small point of technique is crucial to the preparation of most stable B_4H_8 base compounds.

Stronger Lewis bases such as PMe_3 are even more effective in stabilization of borane acids than are the somewhat weaker bases like NMe_3 . The reaction of B_5H_{11} and PMe_3 gives a new hypo-class dibase adduct of B_4H_8 .¹⁹ The equation is:

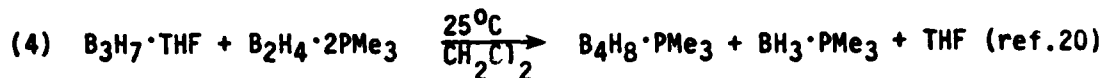


Because the strong base diadduct, $B_4H_8 \cdot 2PMe_3$, is so stable, the monoadduct, $B_4H_8 \cdot PMe_3$, can only be prepared by indirect means. The removal of a base such as PMe_3 from the diadduct²⁰ and the removal of an H^- from the formally analogous compound $[B_4H_8 \cdot PMe_3 \cdot H^-]$ ^{20,21} provide workable routes to $B_4H_8 \cdot PMe_3$. Yields in all cases are over 90%.

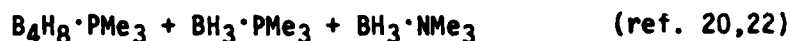
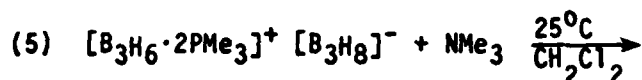


In addition, the monoadduct $B_4H_8 \cdot PMe_3$ can be built up by combination of

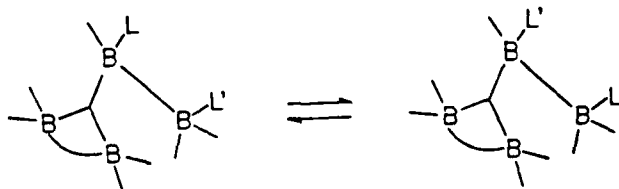
smaller borane units.* Equations for two such processes are:



where THF = tetrahydrofuran,

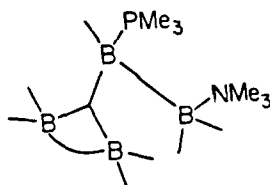


The existence of both $\text{B}_4\text{H}_8 \cdot 2\text{PR}_3$ and $\text{B}_4\text{H}_8 \cdot \text{PR}_3$ suggested that the formation of mono and dibase adducts of B_4H_8 should be a general phenomenon. One can postulate that stronger bases form the dibase adducts preferentially while weaker bases form the monoadducts more easily. This generalization has been verified. The monoadduct $\text{B}_4\text{H}_8 \cdot \text{NMe}_3$ will add one mole of NMe_3 at -40°C to give $\text{B}_4\text{H}_8 \cdot 2\text{NMe}_3$.¹⁷ The second mole of NMe_3 is lost at higher temperatures. Other bases such as NMe_2H , NMeH_2 , and PMe_3 will also add to $\text{B}_4\text{H}_8 \cdot \text{NMe}_3$ to give mixed adducts.²³ As expected, it is easier to add NMe_3 to $\text{B}_4\text{H}_8 \cdot \text{PMe}_3$ than it is to add PMe_3 to $\text{B}_4\text{H}_8 \cdot \text{NMe}_3$. It is suggested that at low temperatures the two different bases appear to exhibit site preference. Base L will add to a different position on B_4H_8 than will base L'. Thus at lower temperatures the reactivity of $\text{B}_4\text{H}_8 \cdot \text{L}$ toward L' can be different than that of $\text{B}_4\text{H}_8 \cdot \text{L}'$ toward



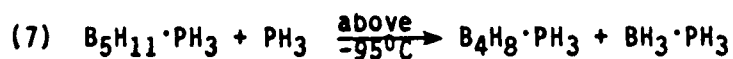
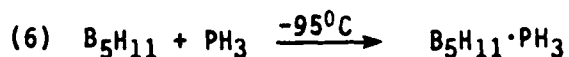
*Preparation of new compounds such as $[\text{B}_4\text{H}_9 \cdot \text{PR}_3]^-$, $\text{B}_2\text{H}_4 \cdot 2\text{PR}_3$ and $[\text{B}_3\text{H}_6 \cdot 2\text{PR}_3]^+ [\text{B}_3\text{H}_8]^-$ are described elsewhere in this report.

L, even though the empirical formulas of the two final diadducts are the same. At higher temperatures the compounds become fluxional such that positional isomers become identical. When a base is lost from the fluxional molecule, the weaker base goes first. For example, $B_4H_8 \cdot CO$ will add PMe_3 at $-40^\circ C$ to give $B_4H_8 \cdot CO \cdot PMe_3$.²⁴ At higher temperatures this compound decomposes to give $B_4H_8 \cdot PMe_3$ plus CO . Direct NMR evidence supporting the existence of low temperature isomers, $B_4H_8 \cdot L \cdot L'$,²⁰ was obtained by studying the diadducts $B_4H_8 \cdot PMe_3 \cdot NMe_3$. The existence of isomers at low temperature and the fluxionality at higher temperatures are clearly seen in $B_4H_8 \cdot PMe_3 \cdot NMe_3$.²⁰ Spectra for the compound suggest that for B_4H_8 , the bases PMe_3 and NMe_3 will bond preferentially to the sites shown.



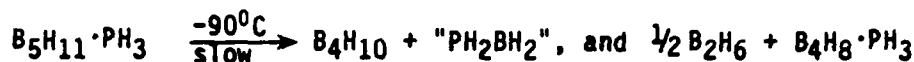
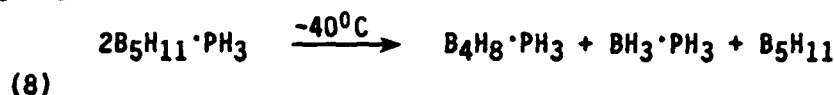
The boron framework of $B_4H_8 \cdot P(NMe_2)_3 \cdot PMe_3$ is not fluxional even at room temperature, but hydrogen atoms do migrate.²⁰

The relatively weak base PH_3 will add directly to B_5H_{11} at $-95^\circ C$.²⁵ This compound reacts with additional PH_3 above $-95^\circ C$ to give the expected monoadduct:

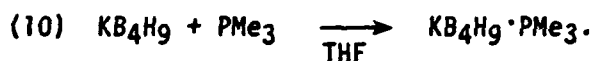
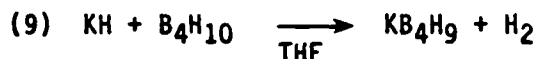


If excess PH_3 is not present, the low temperature B_5H_{11} addition compound,

$B_5H_{11} \cdot PH_3$, decomposes in accordance with the equations:



Writing $B_4H_9^-$ as $B_4H_8 \cdot H^-$ suggests that direct addition of PMe_3 to $B_4H_9^-$ should give the new hypho-class anion $[B_4H_8 \cdot H^- \cdot PMe_3]$. The reaction has been verified.²¹ $P(NMe_2)_3$ will also add to $B_4H_9^-$. The phosphine adducts decompose above $0^\circ C$. An NH_3 adduct exists below $-40^\circ C$.²⁶ All are fluxional. The pertinent equations are:



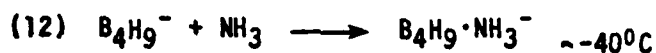
The existence of the compound $KB_4H_9 \cdot NH_3$ at $-40^\circ C$ now explains why the preparation of the diammoniate of tetraborane, $[H_2B(NH_3)_2]^+ [B_3H_8]^-$ is so sensitive to experimental conditions of synthesis. When the synthesis of $B_4H_{10} \cdot 2NH_3$ was first achieved, over 25 years ago, the following experimental points were identified as crucial:²⁷

- (1) The reacting ratio NH_3/B_4H_{10} should NOT exceed 2.
- (2) The reaction must be run in a solvent, preferably Et_2O .
- (3) The reaction mixture must be digested for one to two weeks at $-78^\circ C$.

If these conditions are not carefully observed, a competing set of processes can occur. The pertinent equations are:



then

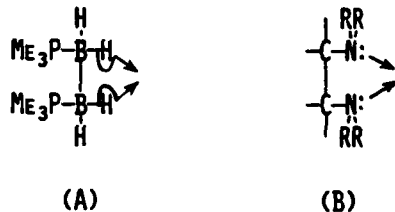


Decomposition

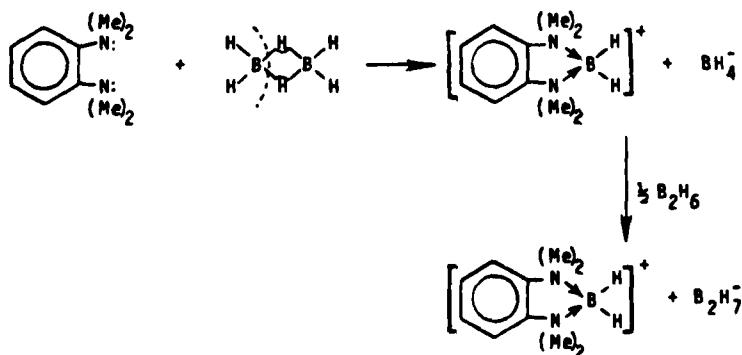
While reaction 11 is reversible, reaction 12 is not and decomposition products are produced. It is interesting that $NH_4^+[B_4H_9 \cdot NH_3]^-$ represents another form of the "diammoniate of tetraborane."

B. Boron Framework Expansion Through the Use of $B_2H_4 \cdot 2PMe_3$.

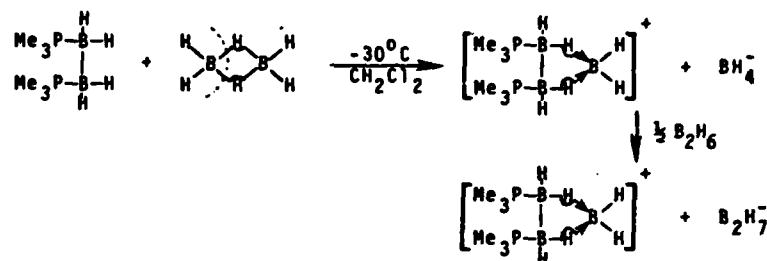
Using an analogy suggested many years ago in this laboratory by Parry and Edwards,²⁸ one notes that a 3-center bridge bond $B \quad H \quad B$ can serve to bind two atoms together just as a 2-center Lewis base + Lewis acid linkage generates an interatomic bond. In terms of this analogy the molecule $B_2H_4 \cdot 2PMe_3$ (A) can be considered to show a formal relationship to diamine molecules (B):



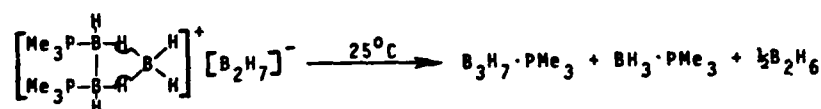
It has been known that some of the diamines, e.g. o-phenylenediamine,²⁹ react with diborane through a non-symmetrical cleavage of the double bridge to give ionic products.



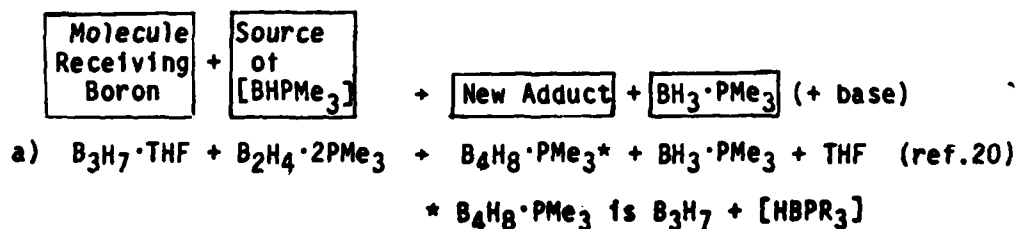
In a completely comparable manner $B_2H_4 \cdot 2PMe_3$ will chelate to a coordination center, and thus it will react with diborane through a non-symmetrical cleavage of the double bridge bond to give an ionic product:

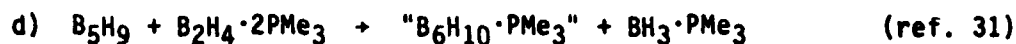
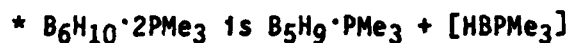
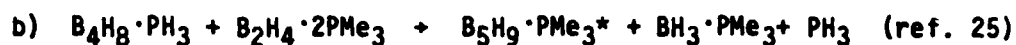


At room temperature the $\frac{1}{2}$ mole of B_2H_6 is released; $B_3H_7 \cdot PR_3$ and $BH_3 \cdot PR_3$ are produced.³⁰

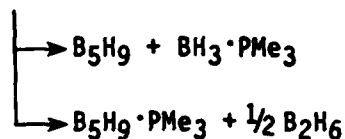
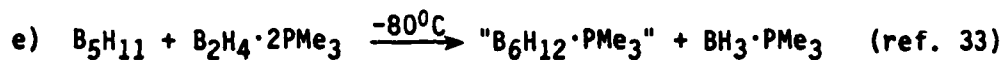


The net effect of this set of reactions is that an $[HBPM_3]$ unit from $B_2H_4 \cdot 2PMe_3$ is added to B_2H_6 to give $B_3H_7 \cdot PMe_3$. In short, the boron framework has been increased by one boron atom. This expansion reaction is quite general for simpler boron hydrides or for borane fragments which are linked to a relatively weak base. In most cases the nature of the intermediate is not as clear as it is for B_2H_6 , but the net addition of an $[HBPM_3]$ unit from the $B_2H_4 \cdot 2PMe_3$ ligand is quite clear. The following equations are illustrative:





The $\text{B}_6\text{H}_{10} \cdot \text{PMe}_3$ appears to be the high temperature form of $\text{B}_6\text{H}_{10} \cdot \text{PMe}_3$ described earlier.³² It decomposes above 25°C.



Although $\text{B}_5\text{H}_9 \cdot \text{PMe}_3$ will add HBPMe_3 , smaller borane adducts of strong bases will not undergo the addition of $[\text{HBPMe}_3]$. For example:



So far the only case where a borane fragment linked to a strong base adds an HBPMe_3 is seen in equation c, where the larger boron fragment $\text{B}_5\text{H}_9 \cdot \text{PMe}_3$ adds $[\text{HBPMe}_3]$, but still retains its attached PMe_3 . Note that, whenever addition of $[\text{HBPMe}_3]$ occurs, the stable species $\text{BH}_3 \cdot \text{PMe}_3$ is also a product. The formation of this very stable substance is one of the driving forces of the $[\text{HBPMe}_3]$ addition reaction.

C. Synthesis of Polyboron Cations.

While polyboron anions are very well known, polyboron cations are not well defined. A number of such polyboron cations have now been prepared in this laboratory and are well characterized. The combination of polyboron cations and polyboron anions to give larger borane derivatives seemed to be a worthwhile avenue for exploration.

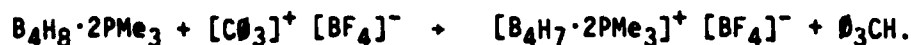
1. $[B_3H_6 \cdot 2PMe_3]^+ [B_2H_7]^-$.

The synthesis of the $[B_3H_6 \cdot 2PMe_3]^+$ cation from $B_2H_4 \cdot 2PMe_3$ by non-symmetrical cleavage of B_2H_6 has been described in part IIB. A similar non-symmetrical cleavage of B_4H_{10} will give $[B_3H_6 \cdot 2PMe_3]^+ [B_3H_8]^-$.³⁰

Another general route to boron cations was suggested by Benjamin³⁴ et al. in 1972. They prepared derivatives of $[H_2BL_2]^+$ of the general form $[H_2BLL']^+$ by use of $[C\equiv C]^+ [BF_4]^-$, the trityl cation. This cation will abstract a hydride ion from $BH_3 \cdot L$ to give $[H_2B \cdot L]^+ [BF_4]^-$ and $C\equiv CH$. If this process is done in the presence of a base, L' , cations such as $[H_2BLL']^+$ are obtained. This general process can be extended to synthesize polyboron cations.

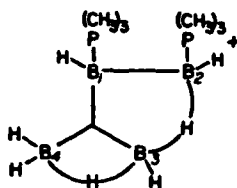
2. The $[B_4H_7 \cdot 2PMe_3]^+$ Cation.

Treatment of the newly synthesized $B_4H_8 \cdot 2PMe_3$ with $[C\equiv C]^+ [BF_4]^-$ resulted in the following reaction:³⁵



The boron containing product is a stable solid at room temperature if air is excluded. It has been characterized by its ¹¹B, ³¹P, and ¹H NMR spectra and

by a boron analysis. On the basis of its NMR spectra the following structure is suggested:



The cation is isoelectronic and isostructural with $B_4H_9^-$ and B_4H_8 L. Presumably the hydrogen atoms of $B_4H_8 \cdot 2PMe_3$ are made quite hydridic through attachment of the two PMe_3 groups to the borane fragment. Under these conditions the hydride anion can be removed by the trityl group. Even other less powerful hydride abstracting species will remove a hydride from $B_4H_8 \cdot 2PMe_3$. For example the following equation also goes as written:



3. Other Polyboron Cations.

Two other cations have been tentatively identified as products of the trityl-hydride extraction procedure. These are formed by the processes:

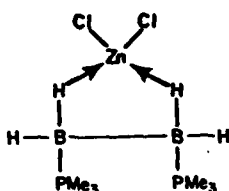


While characterization data are quite strong, more complete characterization is still in progress.

D. The Coordination Chemistry of $B_2H_4 \cdot 2PMe_3$.

In section IIB the compound $B_2H_4 \cdot 2PMe_3$ was compared to a diamine molecule

and it was proposed that a $B \begin{array}{c} H \\ \diagup \quad \diagdown \\ \rightarrow M \end{array}$ three center bridge bond can be used to bind a ligand to a positive center just as a Lewis electron pair can be used. If this premise is adopted, reaction between neutral $B_2H_4 \cdot 2PMe_3$ and metal salts such as $ZnCl_2$ would be anticipated.



The compound has been completely characterized. An X-ray study has been completed. Reports from this laboratory on the $ZnCl_2 \cdot B_2H_4 \cdot 2PMe_3$ complex are now in the literature.³⁶

The coordination of borane fragments to metals through $B \begin{array}{c} H \\ \diagup \quad \diagdown \\ \rightarrow M \end{array}$ bonds is fairly well established for anions. Thus complexes of $B_3H_8^-$ are well recognized^{37,38} and the complex substance $Mn_3(CO)_{10}B_2H_7$ ³⁹ may be considered as a complex of $B_2H_6^{-2}$ in which the normally unstable anion is stabilized by coordination. On the other hand, the ability of a neutral borane adduct to coordinate with a metal had not been demonstrated previously. Other neutral borane adducts such as $BH_3 \cdot PMe_3$ and $B_3H_7 \cdot PMe_3$ did not react with $ZnCl_2$. apparently both the "H.....H chelating bite distance" and the electron density on the hydrogen atoms are important factors in the formation of these chelate coordination compounds. Preferential complex formation may well provide improved routes for the separation of the components in a complex reaction

mixture.

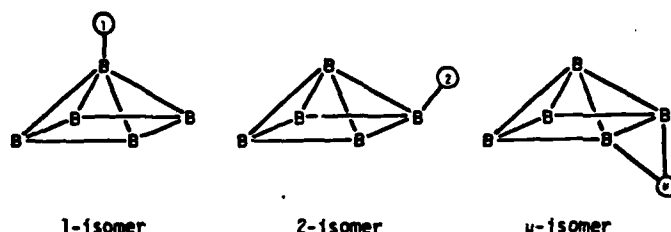
Extensions of the above work are now underway.

E. Miscellaneous Contributions.

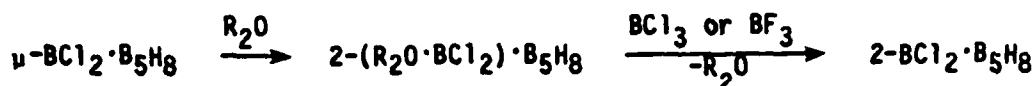
A number of smaller, yet significant, contributions have been made during the course of our investigations under ARO sponsorship. These are enumerated briefly here.

1. Dichloroborylpentaborane(9), $\text{BCl}_2 \cdot \text{B}_5\text{H}_9$.

Three isomers of $\text{BCl}_2 \cdot \text{B}_5\text{H}_9$ are possible depending upon the positions of the BCl_2 group attached to the pyramidal structure of the pentaborane framework. These are 1-, 2-, and μ -isomers as illustrated in the figure.



The 1-isomer was prepared in Gaines' laboratory at the University of Wisconsin⁴⁰ and the μ -isomer was prepared in our laboratory,⁴¹ and both were reported in the same year. The missing 2-isomer is now prepared, and has been characterized.⁴² The steps for the 2-isomer preparation are



The ^{11}B and ^1H NMR spectra and the mass spectral data confirmed the identity of $2\text{-BCl}_2\cdot\text{B}_5\text{H}_8$. Like the μ -isomer, the compound is very sensitive to air. Bromine cleaves the external B-B bond to give $2\text{-BrB}_5\text{H}_8$, and ethylene inserts to form $2\text{-(BCl}_2\text{CH}_2\text{CH}_2)\cdot\text{B}_5\text{H}_8$.

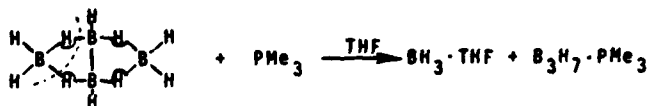
The study of reaction chemistry of both μ - and $2\text{-BCl}_2\cdot\text{B}_5\text{H}_8$ is being pursued. The reaction with diborane is noteworthy. While the resulting mixtures from the treatment of 2-isomer with B_2H_6 consisted of the components which appeared to contain the B_5 framework in their structures, those from the μ -isomer contained substantial amounts of $\text{B}_{10}\text{H}_{14}$.

2. Reaction Chemistry of $\text{B}_3\text{H}_7\cdot\text{PH}_3$.

The reaction chemistry of $\text{B}_3\text{H}_7\cdot\text{PH}_3$ has been compared and contrasted with the previously defined reaction chemistry of $\text{BH}_3\cdot\text{PH}_3$ with NH_3 . In general differences in behavior can be understood in terms of the greater acid strength of B_3H_7 as compared to BH_3 . Details are being published.^{43,44}

3. Anomalies in the Reactions of B_4H_{10} With Bases.

When B_4H_{10} reacts with one mole of PMe_3 in THF one would expect the stronger base, PMe_3 , to combine with the stronger acid, B_3H_7 , and the weaker base, THF, to combine with the weaker acid, BH_3 . The process expected is:

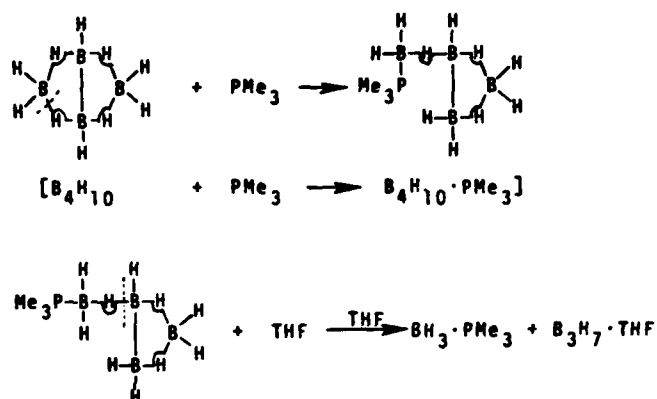


When the process was carried out below -80°C , the products observed were quite the opposite from those expected. The following equation describes our

observations:⁴⁵



It is now clear that the initial set of products, $\text{B}_3\text{H}_7 \cdot \text{PMe}_3$ and $\text{B}_3\text{H}_7 \cdot \text{THF}$ are a result of reaction mechanism; the observations provide support for mechanistic proposals on cleavage of the bridges of B_4H_{10} which were made from this laboratory 27 years ago.²⁷



The resulting initial solution containing $\text{BH}_3 \cdot \text{PMe}_3$ and $\text{B}_3\text{H}_7 \cdot \text{THF}$ undergoes a slow equilibration at room temperature:



The equilibrium constant for this base exchange process was measured and found to be 4 ± 1 at 25°C .

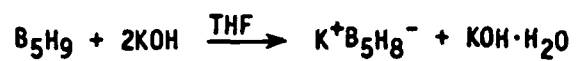
Some related reactions of B_4H_{10} have also been studied.⁴⁵

4. The Deuteration of Triborane Adducts.

The triborane(7) adducts of THF and of NMe_3 react with DCl at -80°C in CH_2Cl_2 to give $\text{B}_3\text{D}_7 \cdot \text{THF}$ and $\text{B}_3\text{D}_7 \cdot \text{NMe}_3$.⁴⁶ The compound $\text{B}_3\text{D}_7 \cdot \text{THF}$ can be converted to NaB_3D_8 ⁴⁷ which can then be converted to $\text{ND}_4\text{B}_3\text{D}_8$. The latter compound has potential interest as a D_2 source.

5. The Deprotonation of B₅H₉ with Solid KOH.

It has been found that B₅H₉ can be deprotonated with powdered, commercial grade KOH in THF at temperatures below -40°C. Yields of KB₅H₈ are nearly quantitative.⁴⁸



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III. Publications and Presentations Resulting From ARO Supported Research

A. Publications

1. "Reactions of Tetraborane(10) with Mono- and Dimethylamine." A. R. Dodds and G. Kodama, Inorg. Chem., 1977, 16, 2900.
2. "Deuteration of Triborane(7) Adducts with Anhydrous Deuterium Chloride." A. R. Dodds and G. Kodama, Inorg Chem., 1977, 16, 3353.
3. "Reactions of Hexamethylenetetramine with Boranes." H. Kondo and G. Kodama, Inorg. Chem., 1979, 18, 1460.
4. "Isolation and Characterization of Trimethylamine-Tetraborane(8)." A. R. Dodds and G. Kodama, Inorg. Chem., 1979, 18, 1465.
5. "Deuterated Sodium Octahydrotriborate(1-)." M. A. Nelson and G. Kodama, Inorg. Chem., 1979, 18, 3302.
6. "Bis(trimethylphosphine) Adduct of Tetraborane(8)." M. Kameda and G. Kodama, Inorg. Chem., 1979, 18, 3302.
7. "Unsymmetrical Cleavage of Boranes by Bis(trimethylphosphine)-Diborane(4). Formation of a Triboron Cation." M. Kameda and G. Kodama, J. Am. Chem. Soc., 1980, 102, 3647.
8. "A Cleavage Reaction of Pentaborane(9). Formation of a New Hypo Triborane Adduct." M. Kameda and G. Kodama, Inorg. Chem., 1980, 19, 2288.
9. "Formation of the 1:1 Phosphine Adducts of Hexaborane(10)." M. Kameda and G. Kodama, Inorg Chem., 1981, 20, 1702.
10. "Triborane Adducts of Phosphine and Methylphosphines." V. L. Bishop and G. Kodama, Inorg. Chem., 1981, 20, 2724.
11. "Deprotonation of Pentaborane(9) with solid Potassium Hydroxide." M. A. Nelson and G. Kodama, Inorg. Chem., 1981, 20, 3579.
12. "Reaction of Pentaborane(11) with Bis(trimethylphosphine)-Diborane(4)." M. Kameda and G. Kodama, Inorg Chem., 1982, 21, 1267.

13. "Preparation and Characterization of (μ -Dichloroboryl)Pentaborane(9)
M. A. Nelson, M. Kameda, S. A. Snow, and G. Kodama, Inorg. Chem.,
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14. "Reaction of Hexaborane(10) with Excess Trimethylphosphine." M.
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15. "Preparation and Characterization of Potassium Nonahydro-
(trimethylphosphine)tetraborate(1-)." M. Shimoi and G. Kodama,
Inorg. Chem., 1983, 22, 1542.
16. "Reaction of Tetraborane(10) with Trimethylphosphine in Tetrahy-
drofuran." M. Shimoi and G. Kodama, Inorg. Chem., 1983, 22, 3300.
17. "Metal Complexes of a Neutral Borane Adducts $B_2H_4 \cdot 2P(CH_3)_3$." S. A.
Snow, M. Shimoi, C. D. Ostler, B. K. Thompson, G. Kodama, and R. W.
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18. "Tetraborane(8) Adducts of Strongly Basic Phosphines", M. Kameda, M.
Shimoi, and G. Kodama, Inorg. Chem., 1984, 23, 3705.
19. "Reactions of Hexahydrobis(trimethylphosphine)triboron(1+)
Octahydrotriborate(1-) with Lewis Bases. Novel Formation of
Tetraborane(8) Adducts." M. Kameda and G. Kodama, Inorg. Chem.,
1984, 23, 3710.
20. "Novel Coordination of a Neutral Borane Adduct to Nickel(0).
Formation of $Ni(CO)_2[B_2H_4 \cdot 2P(CH_3)_3]$ ", S. A. Snow and G. Kodama,
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21. "Synthesis of Heptahydrobis(trimethylphosphine)tetraboron(1+)
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B. Dissertations

1. "Trimethylamine-Tetraborane(8), Methylamine Adducts of Triborane(7) and Related Chemistry." A. R. Dodd, Ph.D. Dissertation, University of Utah, 1980.

C. Presentations

1. "Isolation and Characterization of Trimethylamine-Tetraborane(8)." G. Kodama and A.R. Dodds, 3rd International Meeting on Boron Chemistry, Ettal/Munich, FRG, July 1976.
2. "Reactions of Pentaborane(11) with Methylamines." R. W. Parry and G. Kodama, 3rd International Meeting on Boron Chemistry, Ettal/Munich, FRG, July 1976.
3. "Reactions of Trimethylamine-Triborane(7) and -Tetraborane(8) with Anhydrous Hydrogen Chloride." A. R. Dodds and G. Kodama, 172nd National Meeting, Amer. Chem. Soc., San Francisco, California, September 1976. INOR 90.
4. "Methylamine Adducts of Trimethylamine-Tetraborane(8)." A. R. Dodds and G. Kodama, 173rd National Meeting, Amer. Chem. Soc., New Orleans, Louisiana, March 1977. INOR 48.
5. "Preparation and Properties of Bis(trimethylphosphine)-Tetraborane(8)." G. Kodama and M. Kameda, 33rd Northwest Regional Meeting, Amer. Chem. Soc., Seattle, Washington, June 1978. Paper No. 145.
6. "Phosphine and Methylphosphine Adducts of Triborane(7)." V. L. Bishop and G. Kodama, 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July 1979. Paper No. 39.
7. "Hypho-Tetraborane Compounds Containing Carbon Monoxide and Phosphine." G. Kodama and R. W. Parry, 4th International Meeting on Boron Chemistry, Salt Lake City/Snowbird, Utah, July 1979. Paper No. 45.

8. "Cleavage of Pentaborane(9) by Trimethylphosphine." M. Kameda and G. Kodama, 35th Northwest-5th Biennial Rocky Mountain Joint Regional Meeting, Amer. Chem. Soc., Salt Lake City, Utah, June 1980. INOR 14.
9. "Reactions of Trimethylphosphines Adducts of Diborane(4) with Boranes." M. Kameda and G. Kodama, 2nd Chemical Congress of the North American Continent, Las Vegas, Nevada, August, 1980. INOR 75.
10. "Reaction of Hexaborane(10) with Excess Trimethylphosphine. Formation of "Klado" Borane Compound." G. Kodama and M. Kameda, 182nd ACS National Meeting, New York, NY, August 1981. INOR 15.
11. "Another Form of Ammoniate of Tetraborane(10)." S. A. Snow, G. Kodama, and R. W. Parry. 183rd ACS National Meeting, Las Vegas, March 1982. INOR 139.
12. "Formation and Characterization of Nonahydro(trimethylphosphine)-tetraborate(1-) Ion." M. Shimoï and G. Kodama. 183rd ACS National Meeting, Las Vegas, Nevada, March 1982. INOR 138.
13. "Reactions of Hexahydrobis(trimethylphosphine)triboron(1+) Octahydrotriborate(1-) with Trimethylphosphine and Some Other Lewis Bases." M. Kameda and G. Kodama, 183rd ACS National Meeting, Las Vegas, Nevada, March 1982. INOR 81.
14. "Recent Findings on the Reactions of Lower Borane Compounds." G. Kodama and R. W. Parry, ARO Working Conference on Boranes. Raleigh, North Carolina, May 10-12, 1982.
15. "Preparation and Characterization of Chlorotriborane(7) Adducts of Trimethylphosphine and Phosphine." M. A. Nelson and G. Kodama, 184th ACS National Meeting, Kansas City, Missouri, September, 1982. INOR 59.
16. "Metal Complexes of Bis(trimethylphosphine)-Diborane(4)," S. A. Snow, M. Shimoï, C. D. Ostler, G. Kodama, and R. W. Parry. Fifth International meeting on Boron Chemistry (IMEBORON V), Swansea, Wales, UK., July 1983. Paper No. C48.

17. "Phosphine (PH_3) Adducts of Tetraborane(8) and pentaborane(11)." C. P. Jock and G. Kodama, 7th Rocky Mountain Regional ACS Meeting, Albuquerque, NM, June 1984. Paper No. 67.
18. "Relative Acid Strength of Triborane(7) and Borane(3) as Observed in Reactions of Phosphine Adducts." R. E. DePoy, V. L. Bishop, and G. Kodama, 7th Rocky Mountain Regional ACS Meeting, Albuquerque, NM, June 1984. Paper No. 68.
19. "A New Isomer of Dichloroborylpentaborane(9)." S. A. Snow and G. Kodama, 7th Rocky Mountain Regional ACS Meeting, Albuquerque, NM, June 1984. Paper No. 69.

IV. Participating Scientific Personnel

Robert W. Parry, Distinguished Professor of Chemistry

Goji Kodama, Research Professor of Chemistry

Vicki L. Bishop, Graduate Student, Research Assistant, M.S., 1979

Rosemarie E. DePoy, Graduate Student, Research Assistant

Alan R. Dodds, Graduate Student, Research Assistant, Ph.D., 1980

Arlee Helstrom, Graduate Student, Research Assistant

John M. Higashi, Graduate Student, Research Assistant

Christopher P. Jock, Graduate Student, Research Assistant

Mitsuaki Kameda, Research Fellow

Teddy Martinez, Undergraduate Research Program Fellow

Mansel A. Nelson, Undergraduate Student, Research Assistant, B.S., 1978

Calvin D. Ostler, Undergraduate Student, Research Assistant

Mamoru Shimo1, Postdoctoral Fellow, Research Associate

Sarah Severson Snow, Graduate Student, Research Assistant

Steven A. Snow, Graduate Student, Research Assistant

Laura Sultze, Undergraduate Research Program Fellow

Brian K. Thompson, Graduate Student, Research Assistant

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